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(54) Title: STRUCTURED AQUEOUS LAUNDRY DETERGENT COMPOSITIONS COMPRISING AMINE OXIDES

(57) Abstract

Heavy duty liquid detergent compositions containing an anionic surfactant component and an amine oxide surfactant are disclosed. The anionic surfactant component comprises, by weight of the composition, from about 5 % to 40 % of alkyl sulfates or alkyl polyethoxylate sulfates. The compositions are structured, provide excellent cleaning of soils, excellent softening, and are capable of suspending particles of up to about 200 microns for at least about one month.

droplets or particles in detergent compositions may be determined by optical means or by electronic microscope, such as a transmission or scanning electron microscope.

Therefore, it is an object of the invention herein to provide a structured, aqueous heavy duty liquid laundry detergent composition which provides excellent cleaning and softening benefits and a desirable rheology.

BACKGROUND ART

Amine oxide surfactants have long been known as useful additives in laundry detergent compositions. See U.S. Patent No. 5,075,501; 5,071,594.

SUMMARY OF THE INVENTION

The present invention encompasses a structured, heavy duty liquid laundry detergent compositions having a pH of from about 5 to about 9, at 10% dilution, and comprising, by weight of the composition:

a) from about 10% to about 40% of an anionic surfactant component which comprises, by weight of the composition:
   (i) from about 5% to about 40% of alkyl sulfate or alkyl polyethoxylate sulfates wherein the alkyl group contains from about 10 to about 22 carbon atoms and the polyethoxylate chain contains from 0 to about 15, preferably from 0 to about 5, more preferably from 0 to about 4, ethylene oxide moieties; and
   (ii) no more than about 5% of fatty acids;
b) from about 1% to about 10% of an amine oxide surfactant having the formula:

$$R^1(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2.qH_2O$$

R' is selected from hydrogen, methyl and $-CH_2OH$; R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated and contain from about 8 to about 24 carbons, x is from 0 to about 6, y and z are intergers such that x+y+z is from about 0 to about 10; q is from 0 to about 2; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy;

when x+y+z is 0, R^1 is a hydrocarbyl moiety having chainlength of from about 8 to about 18; when x+y+z is different from 0, R^1 may be somewhat longer, having a chainlength in the range C_{12}-C_{24};

c) no more than about 10%, by weight, of solvents or hydrotropes; and
d) from 0% to about 10% of a suitable electrolyte or acid equivalent thereof;

wherein v is the sedimentation rate of the insoluble; d_s is the density of insoluble to be suspended; d_{fl} is the density of fluid to suspend the insoluble; g is gravity; r is radium of the insoluble; η is viscosity.

According to Stoke's Law, the rate of particle sedimentation is inversely proportional to the viscosity, i.e., the higher the viscosity, the more stable the suspension will be. Thus, a high "zero shear" viscosity is preferred, i.e., for this invention a zero shear viscosity of above about 100,000cp, preferably above about 500,000cp, even more preferably above about 1,000,000cp is desired.

The rheology and the suspending ability of these compositions are believed to be caused by the formation, in the specific compositions of this invention, of a space filling network of liquid crystalline surfactant particles (also known in the art as liposomes or vesicles) having a typical size of about 0.1 to about 10 microns. Moreover, the rheological property of the compositions herein is believed to be due in part to the presence in specific amounts of certain electrolytes, including sodium sulfate and citrate. Without being limited by theory, it is believed that the presence of electrolytes acts to control the size of the liquid crystalline surfactant particles. Thus, the structured nature of the compositions herein are affected by the choice of surfactants and by the amount of electrolytes present. In preferred embodiments herein, the compositions will further comprise from 0% to about 10%, more preferably from about 2% to about 6%, even more preferably from about 3% to about 5%, of a suitable electrolyte or acid equivalent thereof. Sodium citrate is a highly preferred electrolyte for use herein.

The compositions herein contain less than about 10%, preferably less than about 7%, more preferably less than about 5%, by weight of solvents and hydrotropes. Without being limited by theory, it is believed that the presence of solvents and hydrotropes can affect the structured versus isotropic nature of the compositions; compositions containing over about 10% solvents and/or hydrotrope lose the ability to remain in a single "phase", i.e., the composition will appear to separate into two or more layers. By "solvent" is meant the commonly used solvents in the detergent industry, including alkyl monoalcohol, di-, and tri-alcohols, ethylene glycol, propylene glycol, glycerine, etc. By "hydrotrope" is meant the commonly used hydrotropes in the detergent industry, including short chain surfactants that help solubilize other surfactants. Other examples of hydrotropes include cumene, xylene, or toluene sulfonate, urea, C_8 or shorter chain alkyl carboxylates, and C_8 or shorter chain alkyl sulfate and ethoxylated sulfates.

The heavy duty liquid laundry detergent compositions herein contain an anionic surfactant component and an amine oxide surfactant as essential ingredients.

especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 1 to about 15.

Preferred alkyl sulfate surfactants are the non-ethoxylated C_{12-15} primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than abut 65°F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates.

The anionic surfactant component of the present compositions comprises from about 5% to about 40%, preferably from about 7% to about 36%, most preferably from about 10% to about 25%, by weight of the detergent composition, of alkyl sulfates or alkyl polyethoxylate sulfates as described above.

Moreover, the anionic surfactant component herein must comprise no more than about 5% of fatty acids. Most preferably, the detergent compositions herein contain no fatty acids. These include saturated and/or unsaturated fatty acids obtained from natural sources or synthetically prepared. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid.

Amine Oxide Surfactants - The compositions herein also contain from about 1% to about 10%, preferably from about 2% to about 7%, more preferably from about 3% to about 5% by weight of an amine oxide surfactant of the formula:

$$R^1(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2.qH_2O \qquad \text{(I)}$$

In general, it can be seen that the structure (I) provides one long-chain moiety $R^1(EO)_x(PO)_y(BO)_z$ and two short chain moieties, CH_2R'. R' is preferably selected from hydrogen, methyl and $-CH_2OH$. In general R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. When $x+y+z = 0$, R^1 is a hydrocarbyl moiety having chainlength of from about 8 to about 18. When $x+y+z$ is different from 0, R^1 may be somewhat longer, having a chainlength in the range C_{12}-C_{24}. The general formula also encompasses amine oxides wherein $x+y+z = 0$, $R^1 = C_8$-C_{18}, R' is H and q is 0-2, preferably 2. These amine oxides are illustrated by C_{12-14} alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein $x+y+z$ is different from zero, specifically $x+y+z$ is from about 1 to about 10, R^1 is a primary alkyl group containing 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments $y + z$ is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents

ethoxylation of from about 6 to about 12 moles of ethylene oxide per mole of alcohol.

The compositions herein also preferably contain up to about 30%, more preferably from about 1% to about 20%, most preferably from about 1% to about 10%, by weight of a non-citrate, non-fatty acid detergent builder material. While all manner of detergent builders known in the art can be used in the present compositions, the type and level of builder should be selected such that the final composition has an initial pH of from about 5 to about 9, preferably from about 6 to about 8, at a concentration of about 10% by weight in water at 20°C.

Detergent builders are described in U.S. Patent No. 4,321,165, Smith et al, issued March 23, 1982, incorporated herein by reference. Preferred builders for use in liquid detergents herein are described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981, incorporated herein by reference.

Enzymes Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, and cellulases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01% to 1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniforms. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered tradename ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available

Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

The enzymes employed herein may be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species. See Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

NaOH	~4	~4
H20	balance	balance
pH	6.7	7.8
Appearance	Opaque	Opaque
	Suspension	Suspension
Zero Shear Viscosity 10^6cp	2.4	47
Viscosity (20/s) cp	750	1000

*Amine oxide is a mixture of 80% C_{12} alkyl dimethyl amine oxide, 16% C_{14} alkyl dimethyl amine oxide, and 4%C_{16} alkyl dimethyl amine oxide.

The detergent samples are made by the following procedure.

The anionic surfactant paste is first mixed with alkyl ethoxylate, $C_{14-15}EO7$ (if present) according to the formula composition, which is followed by the addition of of sodium hydroxide. Citric acid is added immediately after NaOH to bring the pH to about 5-9 at 10% solution. The amine oxide is then added. Immediately after the addition of the amine oxide, an opaque, lamellar droplet-filled suspension sample is formed. Water and other ingredients are added at the end to complete the formulation.

The compositions of Examples I and II have a viscosity/rheology capable of suspending solids and are stable for more than 30 days.

6. The composition of Claim 5 wherein the anionic surfactant component of the anionic surfactant comprises from 7% to 36% alkyl ethoxylated sulfates.

7. The composition of Claim 6 wherein the anionic surfactant component comprises from 10% to 25% alkyl ethoxylated sulfates.

8. The composition of Claim 7 comprising from 3% to 5% of the amine oxide surfactant.

9. The composition of Claim 1 wherein the amine oxide surfactant is selected from the following: dodecyldimethylamine oxide dihydrate, hexadecyldimethylamine oxide dihydrate, octadecyldi-methylamine oxide dihydrate, hexadecyltris(ethyleneoxy)-dimethyl-amine oxide, tetradecyldimethylamine oxide dihydrate, and mixtures thereof.

10. The composition of Claim 9 comprising from 3% to 5% of dodecyldimethylamine oxide dihydrate, tetradecyldimethylamine oxide dihydrate, hexadecyldimethyl-amine oxide dihydrate, and mixtures thereof.

11. The composition of Claim 1 wherein the weight ratio of anionic surfactant component to amine oxide surfactant is from 2:1 to 3.5:1.

12. The composition of Claim 1 further comprising up to about 10% of an ethoxylated nonionic surfactant and from 1% to 20% of a non-citrate, non-fatty acid detergent builder material.

13. The composition of Claim 1 further comprising an enzyme selected from the group consisting of proteases, amylases, lipases, cellulases and mixtures thereof at a level sufficient to provide from 0.01 mg to 3 mg of active enzyme per gram of the composition.

14. The composition of Claim 1 wherein said composition is capable of suspending particles of up to approximately 200 microns for a period of at least one month.

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 039 451 (PHILLIPS B. M. ET AL.) 13 August 1991 see column 4, line 15 - line 56 see column 5, line 7 - line 10 see column 7, line 31 - line 35 ---	1,5,9
A	US,A,5 075 501 (BORLAND JAMES E. ET AL.) 24 December 1991 cited in the application see column 4, line 53 - column 5, line 18 see claims 1-3,9-16 ---	1,9,10
A	US,A,5 071 594 (BORLAND JAMES E. ET AL.) 10 December 1991 cited in the application see claims 1-4,14-18 ---	1,9,10, 12
A	WO,A,95 05440 (THE PROCTER & GAMBLE CO.) 23 February 1995 see page 6, line 9 - page 7, line 30 see claim 1 -----	1,9,10

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern al Application No
PCT/US 96/15523

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5071594		EP-A- 0421327	10-04-91
		JP-A- 3179096	05-08-91
WO-A-9505440	23-02-95	EP-A- 0713521	29-05-96

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